



Environmental Effects of Dredging Technical Notes



Determination of Total Organic Carbon in Estuarine Leachate Samples

Purpose

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This technical note describes an analytical procedure for determining total organic carbon (TOC) in multiphase leachate samples containing microparticulates, details the techniques used to obtain analytical results and ensure data validity, and presents performance statistics on accuracy, precision, and bias.

Background

Dredging operations of the U.S. Army Corps of Engineers may result in disposal of dredged material in a confined disposal facility (CDF). Dredged material may contain various types of inorganics (metals), oils, and organic contaminants. When placed in a CDF, dissolved organic matter and microparticulates may facilitate leaching of contaminants into surface water or groundwater. Column leach tests under development by the Corps of Engineers provide a controlled laboratory mechanism for simulating the leaching process in a CDF. Collection and evaluation of leachate samples provide quantitative information needed to assess potential water quality impacts of the confined disposal alternative.

Testing of estuarine leachate samples containing colloids and microparticulates requires special analytical techniques. A procedure detailing the determination of TOC concentration in estuarine leachate samples is described in this technical note.

Additional Information

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Introduction

Distinct differences in leaching characteristics of freshwater and estuarine sediments have been observed and documented (Brannon and others 1991; Lee and others 1993a,b,c; Myers and Brannon 1993). Anaerobic leaching of freshwater sediments with distilled-deionized (DDI) water produces aqueous leachate samples relatively free of microparticulates (Brannon, Myers, and Price 1992). Conventional liquid injection procedures (American Public Health Association 1989, U.S. Environmental Protection Agency 1986) for TOC determination are analytically sound for these leachate samples.

Column leaching of estuarine sediments with DDI water initially produces microparticulate-free leachate samples. After leaching several pore volumes, leachate samples containing nonfilterable colloids and nonsettleable microparticulate matter are obtained (Lee and others 1993a,b,c). Analysis of these samples for metals and organic species using standard procedures presents no major obstacles. However, analysis of these samples for TOC using standard techniques has been subject to error due to the nonhomogeneity of the samples and the dispersion of TOC in both water and colloid phases.

Preliminary testing of estuarine leachate samples by a modified ampule method resulted in a fivefold increase in TOC over identical samples tested by standard liquid injection techniques. These highly disparate results indicate that quantitation of TOC in estuarine leachate samples by liquid injection techniques is problematic, and may yield erroneously low results. Separate analysis of liquid and microparticulate phases after filtration is an alternative. However, possible losses during filtration and the attendant problems associated with multiple sample analyses justify the development of an analytical technique for whole sample testing, that is, without microparticulate separation.

The TOC concentration in nonhomogeneous, aqueous-based, multiphased, estuarine leachate samples is more appropriately determined by the modified ampule method described in this technical note.

Sediment Leaching

Two estuarine sediments were tested in this study: Outer Oakland Harbor (Oakland, CA) and Pinole Shoal (Baldwin Harbor, California). Sediments were mechanically mixed under a nitrogen atmosphere, weighed, and loaded into the column leach apparatus described in Brannon, Myers, and Tardy (1994). Leaching tests were performed in duplicate for all sediments.

DDI water was transported to each column in an upflow mode. Water flow rates providing average pore water velocities of about 1×10^{-5} cm/sec were

Sample Preparation

Preparation of Standards, Calibration Curve, and Quality Control Samples

A 50- $\mu\text{g}/\text{ml}$ instrument calibration check standard (ICCS) was prepared by pipetting 5.0 ml Carbon Stock Solution into a 100-ml volumetric flask and diluting to volume with DDI water.

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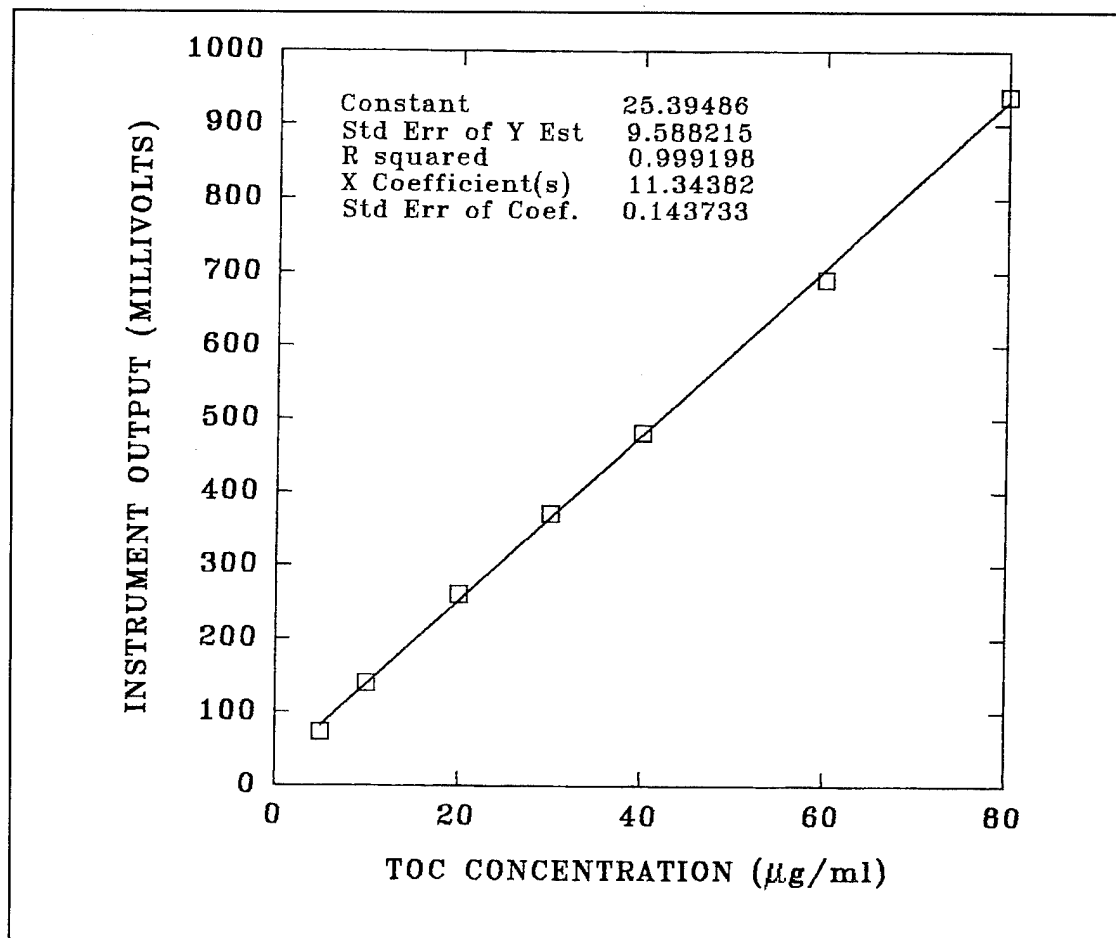


Figure 1. Total organic carbon standard calibration curve

A certified reference material (CRM) (No. 03042 from Environmental Resource Associates) was prepared as instructed in the Certificate of Analysis accompanying the CRM.

Quantitative Analysis of Standards and Samples

An Oceanographics International Corporation model 700 TOC Analyzer was used to quantitate the organic carbon content of samples and standards. After breakage of the ampules on the cutter assembly, the carbon dioxide formed was carried by an inert, nitrogen gas stream to the nondispersive infrared detector and measured. Carbon dioxide detected was a quantitative measurement of TOC in the sample.

Quality Control

Prior to analyzing samples, the instrument was calibrated using a DDI water blank and the 50- $\mu\text{g/ml}$ ICCS. Instrument performance was monitored

throughout the analytical run, by periodically reanalyzing the ICCS. Prior to sample testing, a method blank and QC sample were analyzed. Precision measurements were obtained by replicate analysis of leachate samples at a frequency of 10 percent. Matrix interference was investigated by spiking samples with 0.25 or 0.5 ml of a 50- μ g/ml carbon standard solution at a 10-percent frequency rate. Method accuracy and bias were determined by analyzing the CRM at the beginning and end of each analytical run. Statistical computations (American Public Health Association 1989, Taylor 1987) were used in evaluating chemical measurement data.

Results and Discussion

Performance Characteristics

QC sample analysis results are shown in Figure 2. The center line represents the mean; the two outer lines represent the upper (UCL) and lower (LCL) control limits, or 99-percent confidence level corresponding to ± 3 standard deviations (SD). The two lines closest to the mean line are the upper (UWL) and lower (LWL) warning limits, or 95-percent confidence level (± 2 SD). The mean value for the quality control sample was 41.0 μ g/ml carbon with a standard deviation of 2.22 μ g/ml carbon. One data point is outside the lower warning limit. However, one analysis result outside the 95-percent confidence level and within the 99-percent level is normal, and is expected to occur approximately once in every 20 analyses. At the 99-percent confidence level, no data points are outside the upper or lower control limits. Nearly symmetrical distribution of data points around (19 above and 18 below) the mean value indicates absence of trending toward high or low bias results (Taylor 1987).

Replicate leachate sample analysis results were evaluated to determine method precision. In theory, replicate calculations based on the difference of two measurements (the range) cannot be less than zero since it is the absolute difference between two positive numbers (Dux 1990). In practice, since bias may represent both positive and negative interferences, expression of relative percent difference having positive and negative values permits evaluation of precision, bias, and data distribution.

Relative percent difference (RPD), shown in Figure 3, was calculated using the formula

$$\pm RPD = \frac{\text{Original result} - (\text{Replicate result})}{\text{Mean}} \times 100$$

All resulting data were within the 25 percent upper laboratory acceptance limit (ULAL) and -25 percent lower laboratory acceptance limit (LLAL). Precision calculated from the SD of the results of duplicate sample analyses was 4.5 μ g/ml.

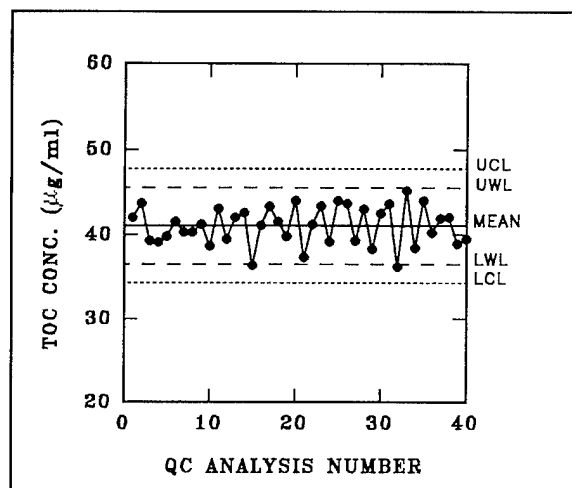


Figure 2. Quality control sample results

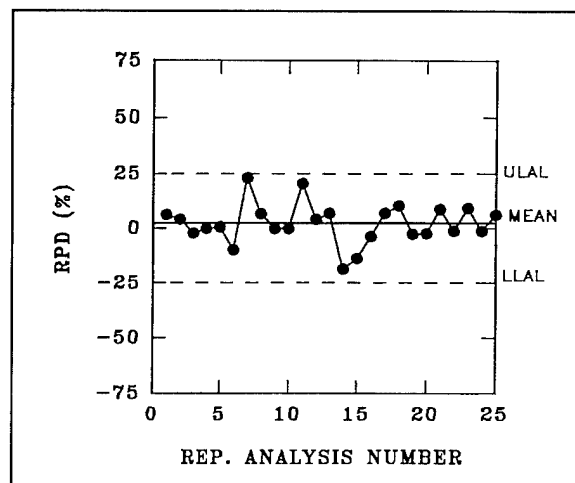


Figure 3. Replicate results for relative percent difference

Percent recovery of spiked samples is presented in Figure 4. Control lines correspond to the mean recovery (97.9 percent) and the ULAL and LLAL values of 125 and 75 percent, respectively. Absence of matrix effects was verified by spike recoveries all within the laboratory acceptance range of 75 to 125 percent, with no data outliers.

Results for the CRM analyzed with this batch of samples are shown in Figure 5. The center line represents the mean value; the outer lines correspond to the upper (UCV) and lower (LCV) control values recommended by the vendor. The mean value for the CRM was 66.6 µg/ml TOC compared with a certified mean value of 67.9 µg/ml with an LCV of 58 µg/ml and a UCV of 78 µg/ml. The standard deviation was 3.2 µg/ml, with a method bias of 1.3 µg/ml, single operator bias of 0.8 µg/ml, and net bias of 1.9 percent. Comparison of the results obtained using this method with the published values for the CRM

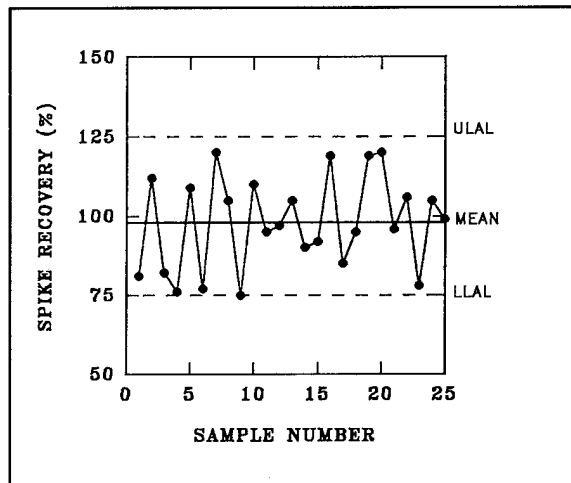


Figure 4. Spike recovery results

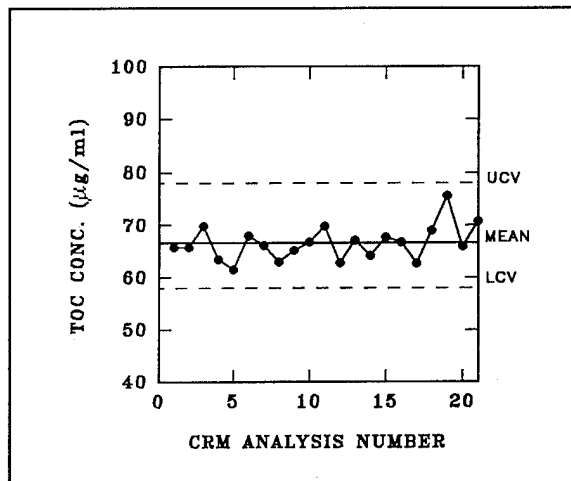


Figure 5. Analytical results for certified reference material

validates the analytical procedure. The CRM data confirm method accuracy and further authenticate the measurement process.

Application

Elution curves depicting TOC released during column leaching of Outer Oakland Harbor sediment with DDI water are shown in Figure 6. TOC concentrations in leachate steadily increased to peak concentrations and then tended to decline. These curves are typical of the elution behavior of contaminants in estuarine sediments when leached with DDI water (Lee and others 1993a,b,c). They show that initial leachate quality is not the worst quality that can be expected when estuarine dredged material is placed upland and leached with low-ionic strength water.

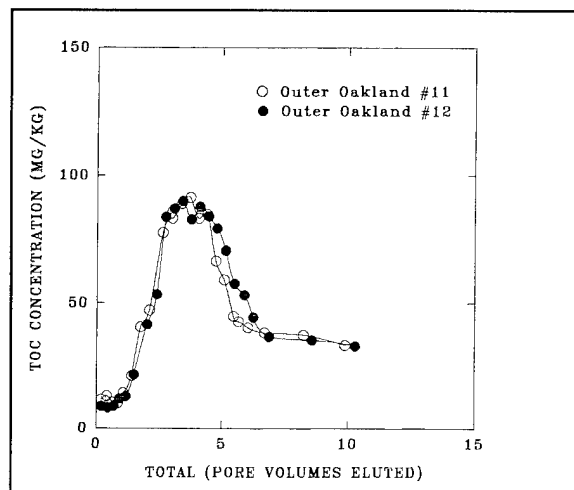


Figure 6. Total organic carbon elution curves

Companion analysis of contaminant concentrations and TOC was not possible in the previous studies by Lee and coworkers (1993a,b,c) because suitable analytical techniques were not available for TOC analysis of samples with significant amounts of nonsettleable microparticulates. Application of the analytical technique presented in this note shows that TOC elution generally correlates to the contaminant elution behavior previously reported and therefore may be instrumental in governing contaminant elution.

Conclusion

The test procedure described in this technical note can be used to make accurate and reproducible measurements of TOC concentrations in estuarine leachate samples. Acceptable bias, precision, and accuracy can be obtained with the procedure. Thus, this method eliminates the need to separately determine TOC in liquid and microparticulate phases of aqueous samples.

In addition to the analysis of leachate samples containing nonsettleable microparticulate matter, the analytical procedure described in this technical note may be applicable to determination of TOC in solid and semisolid materials containing moderate to large amounts of organic carbon. TOC determination in samples of this nature presently requires sample predrying and sieving, which may introduce errors resulting in unacceptable bias, accuracy, and precision results. The procedures described in this technical note eliminate these steps and could provide more accurate and precise results.

References

American Public Health Association. 1989. *Standard Methods for the Examination of Water and Wastewater*, 17th ed., Washington, DC, pp 1-1 through 1-26.

- Brannon, J. M., Myers, T. E., and Price, C. B. 1992. "Leachate Testing of Hamlet City Lake, North Carolina, Sediment," Miscellaneous Paper D-92-5, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Brannon, J. M., Myers, T. E., and Tardy, B. A. 1994. "Leachate Testing and Evaluation for Freshwater Sediments," Miscellaneous Paper D-94-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Brannon, J. M., Myers, T. E., Gunnison, D., and Price, C. B. 1991. "Nonconstant Polychlorinated Biphenyl Partitioning in New Bedford Harbor Sediment During Sequential Batch Leaching," *Environmental Science and Technology*, Vol 25, No. 6, pp 1082-1087.
- Dux, J. P. 1990. *Handbook of Quality Assurance for the Analytical Chemistry Laboratory*, 2nd ed., Van Nostrand Reinhold, New York, pp 39-42.
- Lee, C. R., Brandon, D. L., Tatem, H. E., Simmers, J. W., Skogerboe, J. G., Price, R. A., Brannon, J. M., Palermo, M. R., and Myers, T. E. 1993a. "Evaluation of Upland Disposal of John F. Baldwin Ship Channel Sediment," Miscellaneous Paper EL-93-17, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- _____. 1993b. "Evaluation of Upland Disposal of Oakland Harbor, California, Sediment," Miscellaneous Paper EL-92-12, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- _____. 1993c. "Evaluation of Upland Disposal of Richmond Harbor, California, Sediment from Santa Fe Channel," Miscellaneous Paper EL-93-18, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Myers, T. E., and Brannon, J. M. 1993. "Synopsis of Hamlet City Lake, North Carolina, and San Francisco Bay Area, California, Sediment Leaching Studies," *Environmental Effects of Dredging Technical Notes EEDP-02-17*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Taylor, J. K. 1987. *Quality Assurance of Chemical Measurements*, Lewis Publishers, Chelsea, MI, pp 7-23.
- U.S. Environmental Protection Agency. 1986. "Test Methods for Evaluating Solid Waste (SW-846)," Method 9060, 3rd ed. (Nov 1986 with Dec 1988 revision), Office of Solid Waste and Emergency Response, Washington, DC.